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COMBUSTION DYNAMICS LABORATORY

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February 1, 1968 through April 30, 1968

"COMBUSTION CHARACTERISTICS OF CRYSTALLINE OXIDIZERS"

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Principal Investigator

May, 1968

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1. FOREWORD

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ii. ABSTRACT

The combustion characteristics of crystalline oxidizers
with methyl substitutions have been studied. Methyl, di-
methyl and trimethyl A.P. have burning rates faster than A.P.
itself. Preliminary studies have shown tetramethyl ammonium
nitrate to be the slowest burning (ambient pressure) mono-
propellant yet found; only two-thirds to one-half as fast
as A.P. A portion of the burning rate increase of the
substituted oxidizers is due to the "molecular premixing"
of fuel (methyl and ammonium) and oxidant (ClO_4^-) groups.

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I. Introduction

A fundamental understanding of the combustion characteristics of a range of physical conditions of crystalline oxidizers is important if complete knowledge pertaining to the combustion and atability characteristics of composite solid propallants is to be ettained. This research involves theoretical and experimental studiee of the burning of crystalline oxidizers ranging in physicel form from large single crystals to low bulk density powdars. A strandburner, window bomb and high-speed motion picture photography will be used to obtain burning rates versus pressure, and to record stability of combustion for a variety of particle sizes and pressure (density) packings of selected crystalline oxidizers (i.e., ammonium perchlorate) and analogous compounds. The study of large single crystal burning will remove particle size, shape, and packing factors as complications. Data from low bulk density powder combustion studies, when compared with single crystal data, provides vital information about combustion zone thickness, ignition and conductivity contributions to the overall combustion phenomena. In addition, it is believed that simple combustion teets of powder oxidizer samples can serve as an efficient screening technique for determining whether chemical modifications have increased or decreased the intrinsic burning rate. Crystalline decomposition mechanisms observed during burning will be related to the oxidizer intrinsic burning reta and the basic properties of the oxidizer such as chemical nature, crystal type, and ion sizes. The velidity of the models will be determined by correlation with the experimental date obtained.

II. Propertise of Substituted Ammonium Perchlorates

As dascribed in Quarterly Report No. 2, we have prepared methyl, dimethyl and trimethyl A.P. for comparison with pure A.P.

Table 1 gives the measured crystal densities at 20°C, and also the high temperature density data of Stammler and co-workers[1]. As might be expected, the crystal densities drop as methyl groups are substituted for hydrogens in the ammonium cation. The change per methyl group added becomes less for each addition. Their paper gives an excellent evaluation of x-ray diffraction data, and a discussion of oxidizer phase transitions from theoretical and experimental points of view.
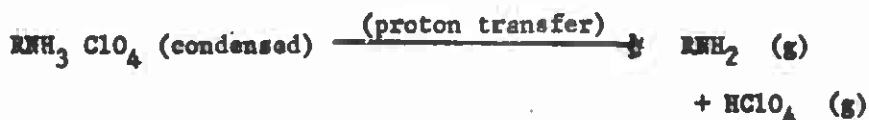
Table 1

Density of Substituted Ammonium Perchlorates

Compound	Density g/cc at 20°C	High Temp.* Density g/cc
Ammonium perchlorate	1.95	1.73 (250°C)
Methylammonium perchlorate	1.65	1.58 (200°C)
Dimethyl ammonium perchlorate	1.48	1.46 (45°C)
Trimethyl ammonium perchlorate	1.43	1.21 (245°C)
Tetramethyl ammonium perchlorate	1.35*(25°C)	----------

*Data of Stammler and co-workers[1].

NOS studies[2] on methylammonium perchlorate, A.P., HAP, and hydrazine perchlorate have shown by the cold matrix-isolation/infrared spectroscopic technique that these oxidizers vaporize by dissociation:

$$RNH_3\ ClO_4\ (condensed) \xrightarrow{\ (proton\ transfer)\ } RNH_2\ (g)$$
$$+ HClO_4\ (g)$$

For hydrazine diperchlorate and guanidinium per-
chlorate the relative vaporization temperatures were cor-
releted with the pK values of the bases in aqueous solu-
tion. Correlations were also made with relative thermal
stabilities.

III. Combustion of Substituted Ammonium Perchlorates

The goal of these studies has been to prepare
crystalline oxidizers releted to state-of-the-art materiels
like A.P.; and then to measure their monopropellant com-
bustion rates. These rates are then to be correlated with
characteristics like chemicel composition, energy release
on combustion, crystal structure, DTA profile and impact
sensitivity.

Quarterly report no. 2 described the tests with
granular $CH_3NH_3ClO_4$ in sample tubes showing its burning
rete to be about 2 1/2 times as fest as A.P. under the
same ambient conditions. Tabla 2 gives the burning rates
of three of these substituted oxidizers compared with A.P.

In conducting these powder burning tests, bulk
density control is critical. It is estimated that the
retio of bulk-to-crystel density should be kept to 0.5^{+}
10% for useful comparisons of burning rate. In comparing
the deta for trimethyl ammonium parchlorete in row 4 with
that in row 5 (of much lower density), the effect of
looser packing in providing a higher charecteristic burning
surface and thus higher measured burning retes can be
easily seen. Tests on the dimethyl and trimethyl materiels
will be continued with gentle packing to increase the den-
sity retio. The quench diamete for these materiels appeers
to ba near 6.0 mm, es compared to 3.5 mm for A.P. Table 3
compares burning rete with seve.al thermochemical veriebles.
We believe the best correlstion will be with specific impulse
for this homologous series. Further testing of the di-
methyl material is most important. Proper density tests
may place its burning rete somewhat below that of MMAP.

Table 2

Monopropellant Substituted A.P. Compounds

Strand Physical Data vs. Combustion

Samples were combustible tubes loaded under dry (10-20% R.H.) conditions with -40 +50 mesh neat oxidizer except where noted.

Crystalline Oxidizer	Loaded Bulk Density, g/cc (sample range)	Crystal Density, g/cc	Density Ratio Bulk/Crystal	Burning rate (in/sec) at 14.7 psia in air	Burning rate Range (no. of Samples)	Sample Tube Diam. (mm.)
NH_4ClO_4	0.99{0.95, 1.05}	1.95	0.51	0.043	+0.002 / -0.002 (10 samples)	6.5
$CH_3NH_3ClO_4$	0.83{0.83, 0.84}	1.65	0.50	0.103	+ .005 / - .034 (4 samples)	6.5
$(CH_3)_2NH_2ClO_4$	0.63{.61, .67}	1.48	0.43	0.132	+ .004 / - .002 (5 samples)	6.0
$(CH_3)_3NHClO_4$	0.65{.63, .69}	1.43	0.45	0.065	+ .013 / - .013 (9 samples)	6.0
$(CH_3)_3NHClO_4$	0.44{.43, .44}	1.43	0.31	0.111	+ .006 / - .003 (5 samples)	6.0
$(CH_3)_3NHClO_4$ (-50+80)	0.44{0.43, 0.44}	1.43	0.31	0.113	+ .003 / - .004 (4 samples)	6.0

Table 3

Monopropellant Burning Rates of

Substituted Ammonium Perchlorates

Crystalline Oxidizer	Burning Rate (in/sec.) at 14.7 psia	Adiabatic Flame Temp. (°K)	Monopropellant Specific Impulse, 66/1 ATM (sec.)	Average Molecular Weight of Combustion Products
NH_4ClO_4	0.043	1403	157.5	27.9
$CH_3NH_3ClO_4$	0.103	3020‡	252.5‡	26.0‡
$(CH_3)_2NH_2ClO_4$	0.132	2130‡	225.0‡	20.9‡
$(CH_3)_3NHClO_4$	0.065	1200‡	200.0‡	18.0‡

‡Data estimated using as basis calculations of Dobbins[4] for CH_2/A.P. mixtures.

Note that whereas flame temp. drops almost 2/3 in going from MMAP to TMAP, specific impulse only drops by 1/5. This is partly because the combustion products molecular weight has dropped by about 1/3, and $I_{sp} \propto \sqrt{T_f/M}$.

Although we have only predicted combustion changes
through the use of substituted A.P.'s in standard propellant,
our attention has been called to an earlier study by Schmidt
and Stammler[3]. Their theories had a basis in very interesting
crystallographic studies in combination with DTA examination
of the substituted A.P.'s. Our theory of rate increase was
based on thermochemical calculations showing greater energy
release and the realization of a fundamental change in com-
bustion reaction conditions (mass transfer) from a hatero-
geneous mixture of fuel and oxidizer--to a "premixed" condition
in which fuel and oxidizer are in each cryatal unit cell.

Schmidt and Stammler have pointed out that a critical
point was reached--with all oxidizers they tested--when the
temperature of the crystal provided sufficient energy to allow
free rotation of the (ClO_4^-) ions. For methyl ammonium
perchlorate (MMAP), this temperature is 180°C as compared
with 240°C for A.P. (see Quarterly Report no. 2, Figures 1
and 2). This free rotation (and phase change) leads to a
reactivity which is embodied in lower DTA exotherms. The
lower exotherms mean final decomposition at lower tempera-
tures, and should lead to higher burning rates. Most
interesting was their propellant burning rate data showing
the effects of methyl ammonium perchlorate and butyl fer-
rocene addition to a standard 71.5 wt.% A.P. oxidizer,
28.5% polybutadiene binder propallant (see Table 4). The
good correlation they obtained between burning rates and
DTA exotherms is of particular interest. This correlation
possibly shows that in a given propellant system when only
small formulation changes are made the relative position of
the DTA exotherm can be an accurate indicator of burning
rate level.

At first glance, one might expect little difference
between the flame temperatures and specific impulse values
of the various test propellants. However, for a $-CH_2-$
(polybutadiene)/A.P. type of system, the maximum energy
relaase is nearer 90% than 70% A.P. The 70% A.P. system
is considerably underoxidized. In fact, the adiabatic flame
temperature of a 90% A.P. system is 3020°K (the same as for
pure MMAP), and the flame temperatura of a 70% A.P. system
is less than 1000°K. This means that almost any hydrocarbon

fuel addition (or its equivalent) will lead to even lower
flame temperatures and energy release. Based on these con-
siderations, it would seem that if flame temperatures had been
held constant in the referenced experiments by increasing the
A.P. fraction when the methyl A.P. was added, the burning rate
increases would have been even greater than those shown in
Table 4.

IV. Impact Sensitivity Test Results

Impact sensitivity was considered the next most
important safety test to differential thermal analysis. With
DTA, we look for exothermic reactions, and in particular, the
final exotherm which usually leads to ignition.

In the impact test, a weighed steel ball of several
pounds is allowed to fall from an adjustable measured height
and impact on a hardened steel sample holder. This fixture
has a movable upper steel plate with protruding striker which
compresses the test sample into a well in a fixed lower plate.
The original potential energy of the ball before dropping is
converted to kinetic energy on dropping and then to thermal
energy, shock waves and strain in the sample and the confining
block. The impact sensitivity values are usually reported in
energy units, always with a well-known compound as a control.
The positive ("fire") test varies from flashing and smoking,
to a loud report. Table 5 shows results for the alkyl sub-
stituted perchlorates. The third column data is taken from
Stammler[1]. It can be seen that there are several ways of
recording sensitivity. A conservative value is the highest
energy input that will not cause a single positive ("fire")
test in ten trials.

Some investigators prefer the higher value, which is
where the first "fire" occurs. Stammler's data uses the energy
input that results in 50% of the sample firing. The trends in
the data and relative values are more important than the
absolute energy values. The agreement between the second and
third columns is considered very good. It can be seen that the
particle size of the material can affect sensitivity consider-
ably (compare ground vs. unground A.P.). Starting with

Table 4

Propellant Burning Rate Modification[‡]

with MMAP and Butyl Ferrocene

Oxidizer System	Butyl Ferrocene Conc. (wt.%)	Burning Rate at 2000 psi (in/sec.)	DTA Exotherm (°C)
AP (Control)	0	0.47	460
AP	4.5%	1.45	230
85% AP + 15% MMAP	4.5%	2.40	190
78% AP + 22% MMAP	4.5%	2.95	180

[‡] Data taken from Schmidt and Stammler[3].

Control propellant is 71.5 wt.% A.P., 28.5 wt.% polybutadiene binder. Butyl ferrocene additions were apparently made with proportionate reductions in oxidizer and binder.

Table 5

Alkyl Substituted Ammonium Perchlorates

Compound	Impact Sensitivity in inch-pounds		
	No Fires in 10 Trials	First Fire Point	50% Fire Point Stammler's Data
$CH_3NH_3ClO_4$	18	22	35
$(CH_3)_2NH_2ClO_4$	28	32	38
$(CH_3)_3NHClO_4$	32	36	43
$(CH_3)_4NClO_4$	--	--	61
NH_4ClO_4 (ground)	--	60	--
NH_4ClO_4 (unground)	--	80	173
AP Propellants	10-20	15-25	--

Note: The first two columns give data from Thiokol-Elkton using a modified JPL impact apparatus. Column 3 (Stammler) gives data from a Bureau of Mines Apparatus.

$CH_3NH_3ClO_4$, there is a regular decrease in sensitivity with methyl substitution. However, all of the alkyl substituted compounds are more sensitive than pure A.P.

Table 6 shows good correlation (inverse relationship) between impact sensitivity and specific impulse in the homologous series of ammonium perchlorates. Flame temperature and Isp estimates were taken from Dobbins[4], except in the case of tetramethyl A.P. where it was felt that the extrapolation would be too great. Neither DTA exotherm nor adiabatic flame termparatures correlated well with the other variables.

V. DTA Comparison: Ammonium Nitrate vs. Tetramethyl

Ammonium Nitrate

It is well known that ammonium nitrate (AN) is difficult to burn, even under pressures of 50-70 atmospheres. Also, ammonium nitrate propellants are difficult to ignite, and a number of additives, notably ammonium dichromate, have been used to promote smooth burning. In the section following, it is shown that although AN will not burn at ambient in the powder burning test, tetramethyl AN burns smoothly. In comparing the DTA curves of these two compounds, it is seen that there are both qualitative and quantitative differences.

Figure I is the DTA plot from 25°C to beyond decomposition for AN. Figure II is the plot for tetramethyl AN (TMAN). Most interesting is the lack of any real endotherm for TMAN. AN shows four distinct phase change endotherms between 40°C and 175°C. It may well be that the combustion difficulties of AN are strongly influenced by the several forms of energy absorption available to the compound before it reaches exothermic temperatures. The AN exotherm is at about 290°C, whereas the TMAN exotherm occurs at about 360°C. With this difference in exotherms, other things being equal, we would expect AN to burn faster and more readily than TMAN. However, referring to our anlaysis of alkyl substituted A.P.

Table 5

Alkyl Substituted Ammonium Perchlorates

Performance Potential vs. Sensitivity

Crystalline Oxidizer	Impact Sensitivity (inch-pounds)	DTA Exotherm (°C)	Adiabatic Flame Temp. (°K)	Specific Impulse (sec.) 68ATM/1ATM
NH_4ClO_4	80	405	1403	157
$CH_3NH_3ClO_4$	22	350	302C	?52
$(CH_3)_2NH_2ClO_4$	32	330	2130	225
$(CH_3)_3NHClO_4$	36	310	1200	200
$(CH_3)_4NClO_4$	55	425	*	*

*Too great an extrapolation of Dobbins' data would be required.

compounds in Quarterly Report no. 2, it may be reasonable
to consider TMAN as a molecular scale mixing of $(CH_2)_n$ and
NH_4NO_3. Such mixtures whether on a particulate or moleo-
uler scale generate high flame temperatures (as compared
with the unsubstituted oxidizer) and thus, even though their
exotherms may be higher, their monopropellant combustion
(ignition and rate) will be enhanced. An excellent refer-
ence on the correlation between DTA plots and crystal cell
transformations is that of Stammler and co-workers[1]. Stam-
mler shows a DTA plot for tetramethyl ammonium perchlorate
and the resemblance to onr DTA plot of TMAN is striking.

VI. Combustion of Substituted Ammonium Nitrate

It was decided to compare pure ammonium nitrate
versus a substituted compound in the combustible tube type
of test used as a screening test in this laboratory. The
substituted compound used was tetramethyl ammonium nitrate
(TMAN). Both powders were -40+50 mesh, at their pour
density (about half of theoretical crystal density), and
were loaded into 4 mm i.d. paper straws.

The samples were 6 to 7 cm in length; they were
burned in ambient air; the AN bulk density was 0.825 g/
cc $\pm$ 0.025, and the TMAN bulk density 0.545 g/cc $\pm$ 0.105.
A minimum of five samples each were burned.

Table 7

Substituted AN Combustion

Oxidizer	Burning Rate in/sec at 14.7 psia	Rate Range
A.P. Control	0.033	+ 0.0015 - 0.0018
Ammonium nitrate	Would not burn	------
Tetramethyl ammonium nitrate	0.022	+ 0.005 - 0.003

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FIGURE II

SAMPLE: Tetramethyl AN
(CH₃)₄ NNO₃

ORIGIN: Eastman Org.Chem.

SIZE: Micro

REF: Class bead

RATE: 20°C/min.

START: 39°C.

ATN. N2

SCALE
SETTING: 50°C/in.
1°C/in.

RUN NO: TMAN

DATE: Mar. 29, '68

OPERATOR: KYC

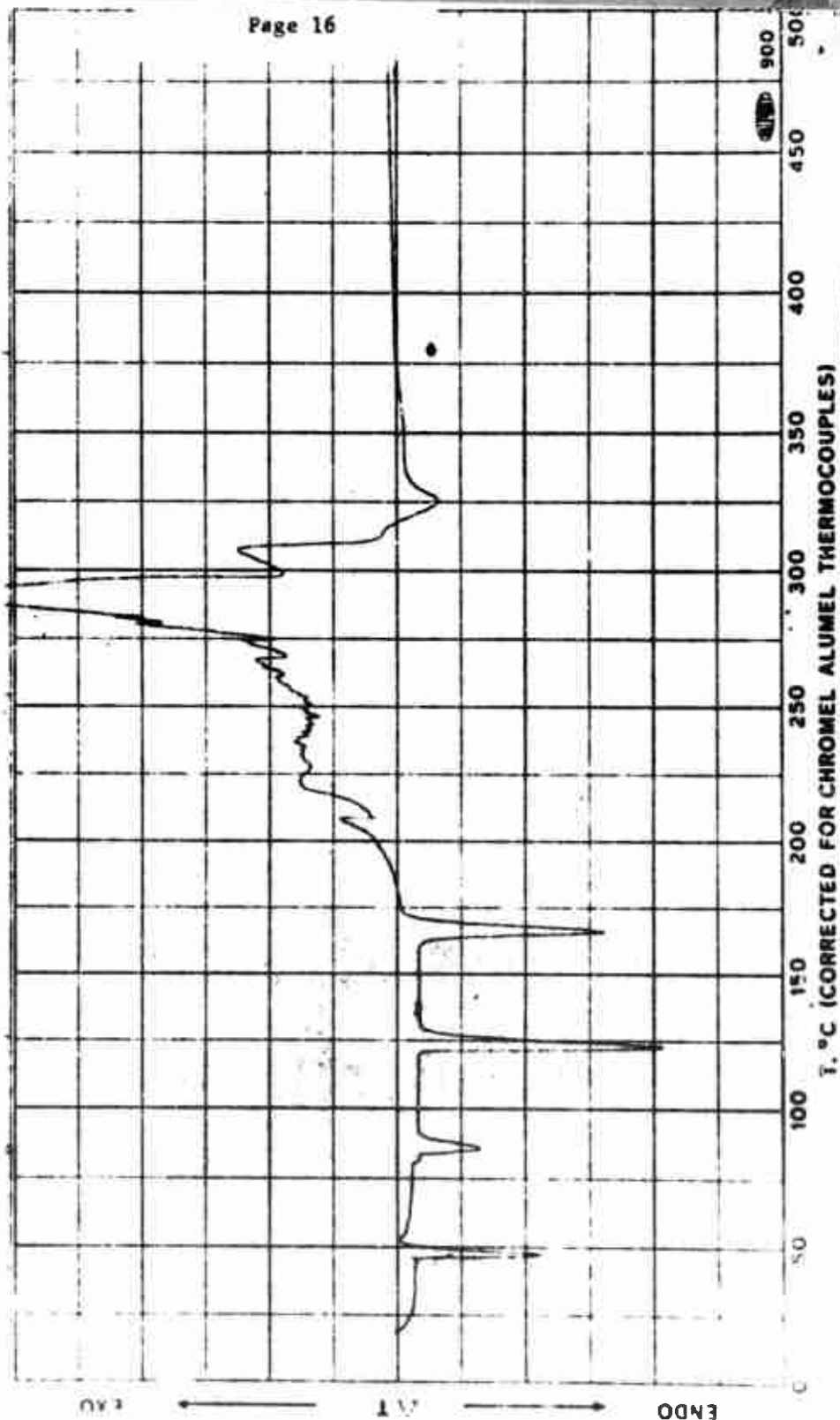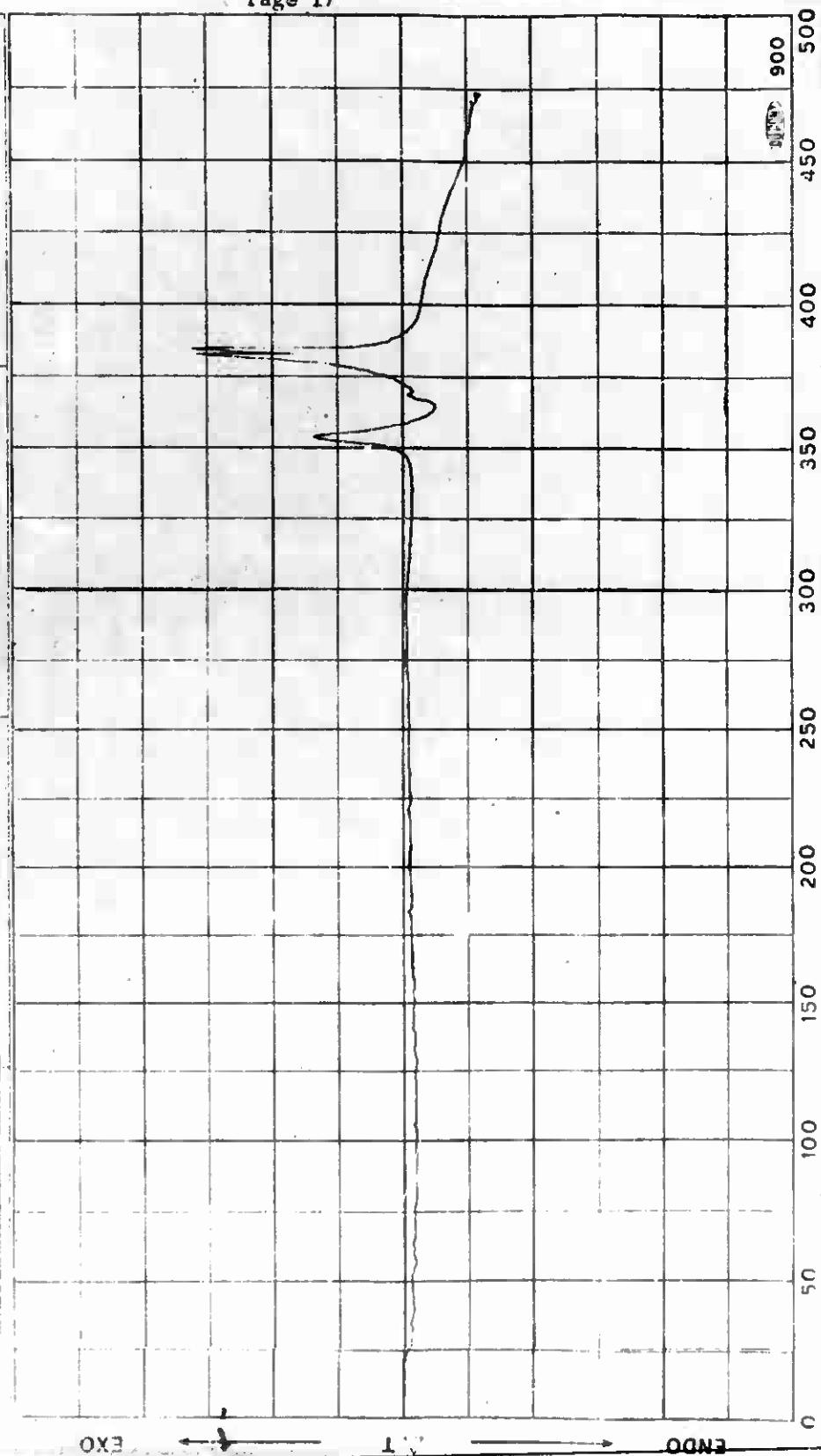As shown in Table 7, the AN samples would not burn,
and the TMAN burned one-third slower than the A.P. control.
TMAN burned with a smooth steady flame and is the slowest
burning monopropellant we have found thus far. The alkyl
substitution converts AN to a monopropellant.

VII. Conclusions

1. Methyl substituted ammonium oxidizers burn
faster than the unsubstituted compounds.

2. In pure substituted perchlorate and nitrate
oxidizer combustion, the faster burning appears to be
partly due to the greater energy release provide by a
better balance of oxidizing and reducing species.

3. Impact sensitivity is directly correlated with
specific impulse in a homologous series.

4. The faster burning attributable to a "molecular
premixing" of reducing and oxidizing species is demonstrated
when propellants having lower energy, but containing a portion
of methyl substituted oxidizer, show a significant burning
increase over reference propellants.

5. When comparing similar propellants, DTA exo-
therms correlated well with burning rate. This is not true
for the pure oxidizer burning rates.

VIII. Future Work

1. The dimethyl A.P. granular oxidizer burning
rate will be determined at higher bulk density.

2. Further attention will be given to quench
diameters and the phenomenon of unstable (pulsating) com-
bustion.

3. Attempts to produce large single crystals of
divalent cation doped A.P. will be continued.

IX. References

    1. M. Stammler, R. Bruenner, W. Schmidt and D. Orcutt, "Rotational Polymorphism of Methyl Substituted Ammonium Perchlorates", pp. 170-189, <u>Advances in X-Ray Analysis</u>, Vol. 9, Plenum Press, 1966.

    2. Naval Ordnance Station, Indian Head, Md., "Chemistry Research, Quarterly Progress Report", January 20, 1967, Report No. TMR 245.

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    4. T. O. Dobbins, "Thermodynamics of Rocket Propulsion and Theoretical Evaluation of Some Prototype Propellant Combinations", WADC TR-59-757, Wright Patterson Air Force Base, Ohio (December, 1959).

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13. ABSTRACT

The combustion characteristics of crystalline oxidizers with methyl substitutions have been studied. Methyl, dimethyl and trimethyl A.P. have burning rates faster than A.P. itself. Preliminary studies have shown tetramethyl ammonium nitrate to be the slowest burning (ambient pressure) monopropellant yet found; only two-thirds to one-half as fast as A.P. A portion of the burning rate increase of the substituted oxidizers is due to the "molecular premixing" of fuel (methyl and ammonium) and oxidant (ClO_4^-) groups.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Combustion						
Solid Oxidizers						
Monopropellants						
Ammonium Perchlorate						
Methyl Ammonium Perchlorate						
Dimethyl Ammonium Perchlorate						
Trimethyl Ammonium Perchlorate						
Tetramethyl Ammonium Nitrate						
Burning Rate						
Quenching Diameters						
Combustion Stoichiometry						